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Thermal Stability Evaluation of Diamond-like Carbon for Magnetic Recording Head Application using Raman Spectroscopy

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Abstract

Diamond-like carbon (DLC) films were deposited on magnetic recording heads using filter cathodic arc for improvement of tribological property and corrosion protection. To increase the areal density of magnetic storage, the thickness of DLC film has to be decreased to less than few nanometers. In addition, the heat occurred at the head-disk interface during the operation can impact on the properties and protective performance of DLC films. In this work, the effect of heat on the properties of DLC films was investigated by visible Raman spectroscopy. The Raman spectra of DLC film as a function of heating temperature and time were carried out. The Raman spectra revealed that the degree of graphitization of the DLC films increased with increasing of temperature and time. The relative Raman intensity was found to decrease with possibility of sp^3/sp^2 ratio decreasing in the films. It can be concluded that the thermal stability of DLC film degraded at high temperature environment.

Keywords: Diamond-like carbon; DLC; heating effect; Raman spectroscopy

1. Introduction

Diamond-like carbon (DLC) films are a form of amorphous carbon that contains a significant fraction of sp^3 bonds. They are well known for their superior physical and chemical properties [1-3]. To date, DLC with the highest fraction of sp^3 bonding has been deposited form a filtered cathodic arc (FCA) or

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mass selected beam of C^+ ions for a solid carbon source [2]. To achieve a high areal density system, DLC overcoats on magnetic recording head have to meet the criteria of corrosion and wear resistance at the thickness less than 2 nm [3]. Unfortunately, previous studies have shown that DLC films cannot retain their superior characteristics at higher temperature because of the irreversible change in the structure, which limits the application of these films [4]. Normally, Raman spectroscopy is used to probe the quality of DLC films due to its ability to distinguish between different bonding types and domain sizes [6]. By means of Raman spectroscopy, for hydrogenated-DLC films at more than 200°C result the effusion of hydrogen, the conversion of sp^3 bonds to sp^2 bond and the loss of diamond-like properties [4]. Raman spectra also revealed that the degree of graphitization of the Ti-doped DLC thin film was increased from 25 to 600°C and microstructure of the films is converted to a nano-crystalline graphite structure [1]. Other studies of thermal stability of DLC-H film and DLC-doped film also show agreement with the previous studies. The cluster size decreased when the annealed temperature increases and the graphite crystallize size of DLC-H is larger than as-deposited one. Thermal annealing results in the graphitization conversion from C-C sp^3 bonded carbon to C-C sp^2 bonded carbon when heating up to 400 °C [5].

The purpose of this paper is to investigate the thermal stability of DLC film deposited from filtered cathodic arc technique on the magnetic recording head application. The roles of heating in property of DLC films is discussed in term of heating-induced changes in the structure of the films using visible Raman spectroscopy at 514.5 nm of Ar^+ ion gas laser.

2. Process condition and experiment setup

2.1. Process condition

The set up for DLC films deposition consists of the single chamber equipped with two RF ion beam sources, 350 mm diameter etch source and 210 mm diameter deposition source with dished ion beam focusing grids ion beam sputtering, and FCA source with 90 deg curvilinear magnetic solenoid filter. The magnetic recoding heads were mounted on the square pallet and seated on the automated substrate fixture which able to tilt and rotate during deposition. The 2 inches diameter Ta coupon is mounted at the center of pallet for in-situ thickness monitor and control. Two multi-wavelength JA Woolam ellipsometers were being performed for separate monitoring seed layer and DLC deposition.

2.2. Film deposition and annealing treatment

DLC films were deposited from a filtered cathodic arc (FCA) to a thickness 0.85 nm on magnetic recording head which consists of alumina titanium carbide and the stacking of other thin film material i.e. NiFe, Al_2O_3, etc as magnetic recoding device. 0.65 nm of a-Si seed layer was sputtered prior to DLC coating to provide a strong adhesion [2]. Ion beam etching with low energy Ar^+ ion was used to achieve surface cleanliness before thin film deposition.

In order to investigate the thermal stability of deposited films, thermal annealing was performed by increasing temperature up to 500 °C for 3 hr with temperature ramping rate at 1.6 °C per minute. Then films structure is verified by collecting Raman spectra after finish each annealing condition.

2.3. Structure characterization of the films

Raman spectroscopy is the best way to obtain the detailed bonding structure of DLCs. Raman is widely used as a non-destructive way to characterize the structural quality of carbons [7]. This method can distinguish the bonding type, domain size, and sensitivity to internal stress in amorphous and

nanocrystalline carbon films. Raman spectra are usually discussed in the context of short distance ordered sp^3 and sp^2 bonds [8].

In this study, Raman backscattering spectra of DLC films were collected on a Renishaw in Via Reflect Raman spectrometer at 514.5 nm of Ar^+ ion gas laser. The incident power on the sample surface is approximately 4 mW from the applied output power of 20 mW and 50X objective lens. The scan range was from 1100 to 2000 cm^{-1}. Raman spectra were fitted using Gaussian profile to obtain smooth curves and with two Gaussian-Lorentzian function corresponding to the G peak and D peak. The G peak is due to the band stretching of all pairs of sp^2 atoms in both rings and chains, and it always lies in the range of 1500 – 1630 cm^{-1}. So, it occurs at all sp^2 sites. The D peak is due to the breathing modes of sp^2 atoms in rings. This mode is forbidden in perfect graphite and only becomes active in the presence of disorder [6].

3. Result and discussion

The microstructure of the DLC films was determined using Raman spectroscopy, which is frequently applied to measure the microstructure of carbon-based material [4]. The Raman peak composed of D and G component. Ferrari and Robertson have suggested that the G and D peak are due to the sp^2 only. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chain reflecting the zone center E_{2g} mode of the perfect graphite. This mode does not require the presence of six fold rings, and so it occurs at all sp^2 sites not only those in rings. The D peak is due to the breathing modes of A_{1g} symmetry involving phonons near the K zone boundary and only becomes active in the presence of disorder [8].

Table 1. Summary of Raman spectra of each annealing condition

Annealing condition	G position (cm^{-1})	D position (cm^{-1})	FWHM of G peak (cm^{-1})	Id/Ig
As-deposited	1530	1445	149	0.404
200C, 3 hr	1551	1451	142	0.795
300C, 3 hr	1561	1448	129	0.938
500C, 3 hr	1599	1430	104	1.095

Figure 1 and 2 present the evolved Raman spectra of DLC films that were annealed from room temperature up to 500 °C for 3 hr.

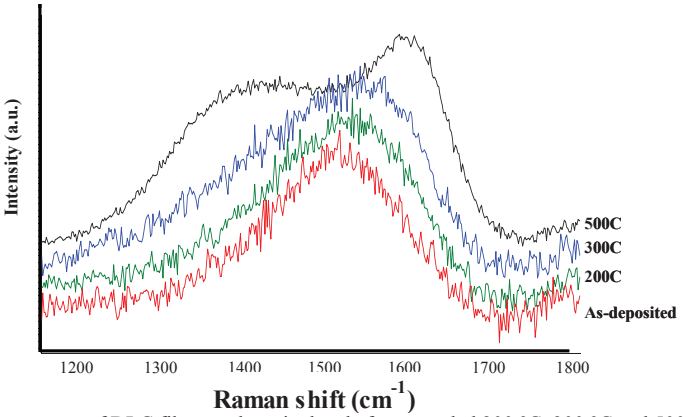

Fig. 1. Raman spectra of DLC films as-deposited and after annealed 200 °C, 300 °C and 500 °C respectively

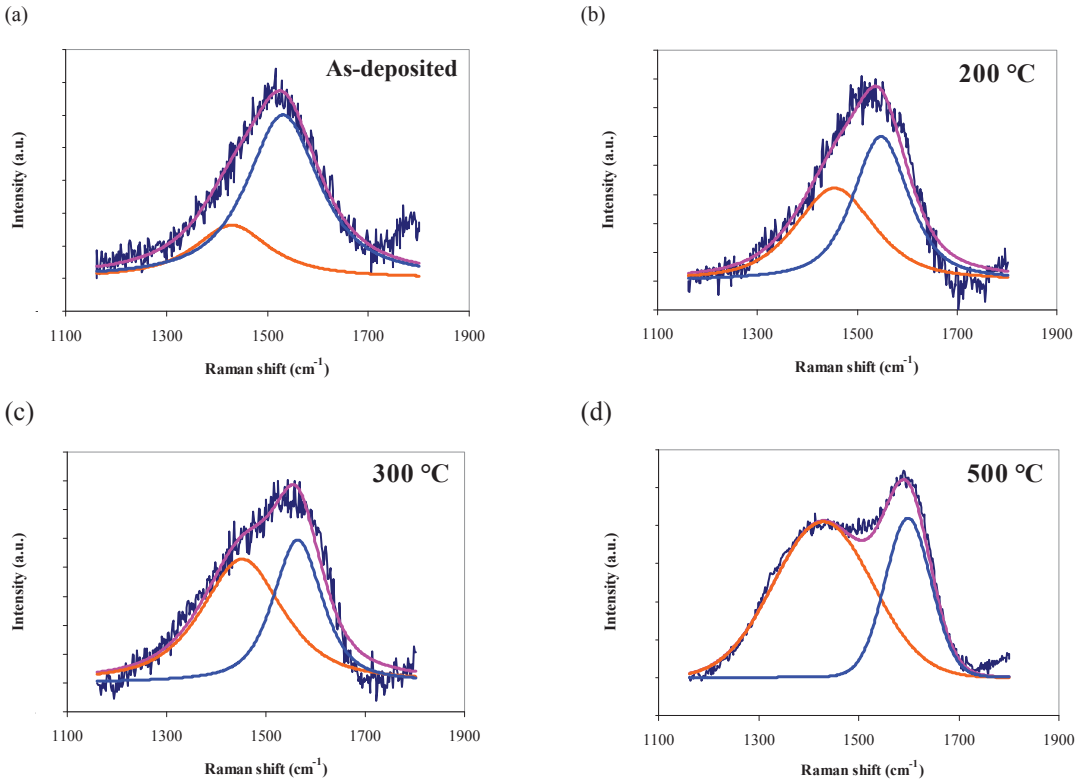

Fig. 2. The fitted Raman spectra of DLC films; (a) as-deposited; (b) after annealed 200 °C; (c) after annealed 300 °C; (d) after annealed 500 °C

The G peak position was shifted to higher frequency after annealing. Ferrari and Robertson verified that high temperature annealing complete stress release induced minimal structural changes in ta-C. The G peak of ta-C is shifted in 514-nm Raman spectra which only be fully explained by contribution of olecfinic sp^2 groups whose has higher vibration frequencies lie above the graphite band limit [6].

Ferrari and Robertson modeled G position and ratio of D peak intensity and G peak intensity (Id/Ig) relationship into 3 different stages called three-stage model corresponding to different forms of carbon that can evolve from single crystal graphite → amorphous carbon → tetrahedral amorphous carbon (ta-C) [6]. For ta-C, the region of interest in term of G position and Id/Ig trend with sp^3 content is between the a-C and ta-C region.

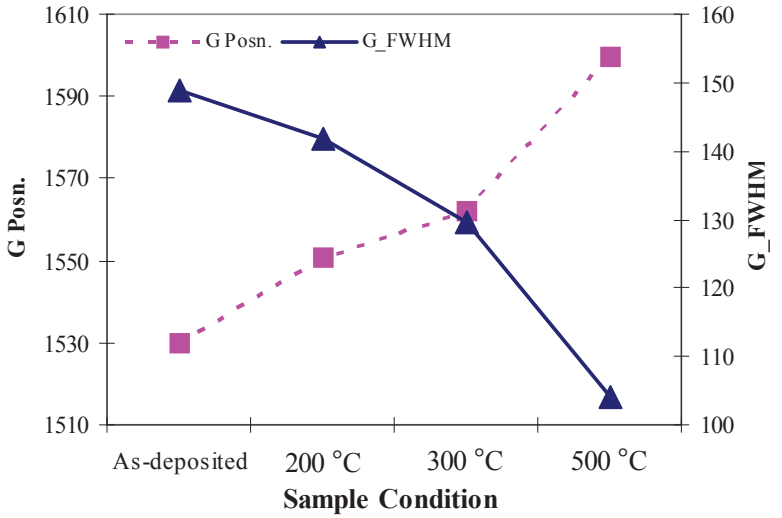

Fig. 3. The plot of G peak position and FWHM of G peak of DLC films as-deposited and annealed at 200 °C, 300 °C and 500 °C

Figure 3 reveals that the full width haft maximum (FWHM) of G peak decreases as annealing temperature increases. The width of the G and D peaks scales with disorder. The FWHM of G peak varies in a power law fashion with microcrystalline size, La, which suggests that FWHM of G peak drops with increasing of La [7].

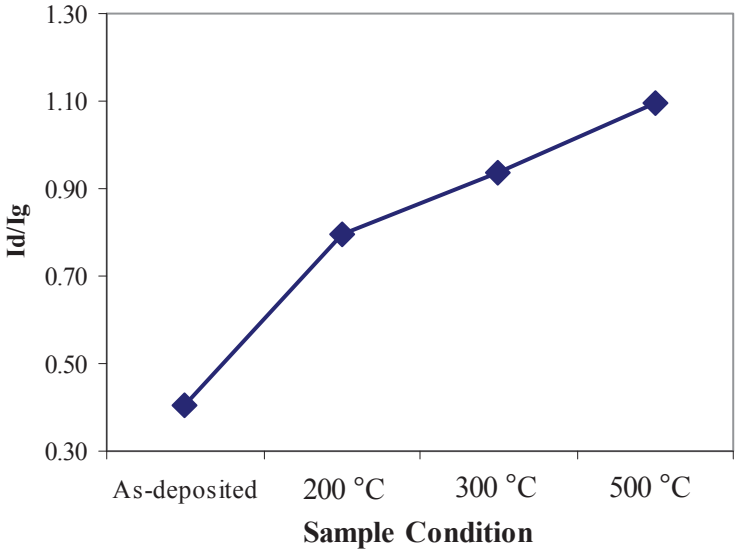

Fig. 4. The plot of intensity ratio of D peak to G peak (Id/Ig) of DLC films as-deposited and annealed at 200 °C, 300 °C and 500 °C

Figure 4 shows that the Id/Ig is also a function of the annealing temperature. The Id/Ig is monotonically increases from 25 to 500 °C. The observed changes of Id/Ig and G position as function of annealing temperature between room temperature to 300 °C may not necessarily only due to conversion of sp^3 to sp^2 bonding. In contrary, as observed and commented by Ferrari et al., the annealing after deposition flavors clustering of sp^2 sites into fairly ordered aromatic rings [6].

However, there is the possibility of conversion of sp^3 to sp^2 on the part after 500 °C annealing due to the significant change in G position, FWHM of G peak, and Id/Ig. All parameters support the idea of phase conversion and increasing of degree of graphitization of DLC film. During the study, surface of films was inspected under microscope which shows film after anneal at 500 °C is significant darker than other conditions and cannot measure the optical constant by ellipsometer. In additional, the G peak and D peak was significant splitted from each other after 500 °C. Base on results of this study as abovementioned suggests that the further verification of DLC films properties are needed to better explains the changes in microstructure which affect the thermal stability of DLCs deposited by FCA technique for magnetic recording head application.

4. Conclusion

In summary, annealing causes the shift of G peak position which is due to the change of sp^2 configuration from ring to olefinic groups. The FWHM of G peak; directly scales of disorder and inversely related to microcrystalline size, La, decreases with an increasing of annealing temperature. The change of intensity suggesting that there is a increasing of sp^2 fraction and order. And from the annealing condition and Raman spectra of this study, Id/Ig reveals the increasing of sp^2 cluster size and the ordering of sp^2 phase in ring. There is no clear relation between Id/Ig or G position of sp^3 fraction. Only the general visible Raman is not direct measurement to get sp^3 content. The additional independent assessment of the sp^3 fraction is needed. The annealing at 500 °C for 3 hr results the significant separation of G peak and D peak which clearly seen in Raman spectra and this is possibly due to phase transformation.

Regarding the information from Raman spectra, the DLC films was changed under high temperature and significant transformation in microstructure at 500 °C which may affect a decreasing in superior properties of DLC films. The optical, mechanical and other properties of DLC films under high temperature conditions need to be studied to gain the better understanding.

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